Boffin Access

Open Access Journal | Volume: 1.1

Journal of Water technology and Treatment methods

ISSN 2517-7427

Synthesis of Silicon Nitride from Rice Husk and Sugarcane Bagasse Ashes

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Abstract

Silicon nitride (Si_3N_4) SNA, SNB, SNC and SND were synthesized by hydrothermal process at temperature of 100°C, 150°C, 200°C and 300°C using Rice Husk Ash (RHA) and Sugarcane Bagasse Ash (SBA) respectively. The percentage of silica ranges from 90.10 to 94.19 with minute impurities.Based on their infrared spectra, for SNA absorption band at 470.6 cm-1 is attributed to Si-N (stretching), which were also observed with SNB, SNC and SND, a weak band at 671.2 cm^{-1} which is characteristic of a silicon nitride Si-N-Si stretching vibration was observed, for SNC, peak at 574 cm^{-1} attribute to α-silicon nitride, as temperature increases the spectrum becomes sharper. X-ray diffraction pattern indicates that SNA material contained 64.6% α-phase and 27.8% β-phase silicon nitride. Therefore, rice husks and sugarcane bagasse have great potential as a raw material for producing Si_3N_4, by the hydrothermal method

Keywords

Silicon nitride; Rice husks; Sugarcane bagasse

Introduction

Silicon nitride (Si_3N_4) is an important ceramic material used for various applications, due to its superior mechanical and electrical properties at elevated temperatures.This material exhibits high quality and hardness, magnificent high temperature and imperviousness to creep, oxidations and thermal shock and as such can be widely used in future [1]. The preparation of silicon nitride (Si_3N_4) from rice husk was initially reported in a US patent in 1974 where the reaction temperature was somewhere between 1100°C and 1350°C [2]. Silicon nitride powders could be prepared up from rice husk at temperatures somewhere around 1260°C and 1500°C under a nitrogen (ammonia) atmosphere. In the past few decades, rice husks picked up fame for specialists on account of its high SiO_2 content, which have altogether enlarged the utilization of rice husks. At present, rice husks can be utilized as crude materials for the generation of silicon, silica, silicon carbide, silicon nitride, silicon tetrachloride and zeolite [3]. Sugarcane bagasse contains 9.78 % of silica and 90.22% of carbon, as compare torice straw which contains 36.14 % of silica and 63.86 % of carbon [4]. One major advantage of using rice husks is that, silica and carbon present in the husk is already in intimate contact and homogeneously mixed with high specific surface area [5]. This would influence the response energy in a positive way and cause the reaction to happen more effortlessly than the mechanical blending of commercial silica and carbon powders. The use of these materials to produce high value product will help to reduce their polluting effects. Rice husk has been used to produce silicon nitride but it lacks excess carbon, which is used as oxygen sink to form CO gas and reduce the oxygen on the powder surface. On the other hand, rice husks usually contain high amounts of impurities, which ends up affecting the product properties and/or produced phases.

Si_3N_4 powder is produced mainly by Carbothermal nitridation of silica (SiO_2) [6].

$$3SiO_{2(s)} + 6C_{(s)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 6CO_{(g)}$$

However, despite the extensive studies, the production of silicon nitride from rice husk has not been commercially implemented because of the problem associated with impurities as well as the very long reaction time required [7]. Synthesis of the α-phase is improved by increasing the partial pressure of CO in the vicinity of the sample [8]. Chen, (2008) used rice husk in the synthesis of silicon nitride and silicon carbide by hydrothermal process [9]. In this study, we used rice husk ash as a source of silica, and sugarcane bagasse ash as a source of carbon in the synthesis of silicon nitride by hydrothermal process.

Materials and methods

Rice husks were provided by Euros rice millers in Kirinyaga County, Mwea west district,

Article Information

DOI: 10.31021/jwt.20181106
Article Type: Research Article
Journal Type: Open Access
Volume: 1 **Issue:** 1
Manuscript ID: JWT-1-106
Publisher: Boffin Access Limited

Received Date: November 01, 2017
Accepted Date: December 15, 2017
Published Date: January 22, 2018

Citation: Abdulhameed A, Mbuvi HM, Changamu EO, Maingi FM. Synthesis of silicon nitride from rice husk and sugarcane bagasse ashes. J Water Technol Treat Methods. 2018 Jan;1(1):106

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Kenya. They were washed several times with distilled water to remove soil and dust, dried in an oven at 100°C for 2 hrs then burnt in a furnace at 800 °C in the presence of air for 3hrs to obtain ash [9]. The sample was allowed to cool, crushed and stored in laboratory for further use. Sugarcane bagasse was obtained from a juice making shop at Kahawa Wendani, Nairobi, Kenya. They were washed several times with tap water followed by distilled water to remove impurities, dried in an oven at 100°C for 2hrs and then heated in a furnace at 500°C for 30 minute to obtain ash [10]. The sample was allowed to cool and stored in laboratory for further use.

Hydrothermal process

The materials used for the hydrothermal reactions were Rice Husk Ash (RHA) as the source of silica, NH_4OH, HCl and sugarcane bagasse as carbon source. NH_4OH (28%), served as a source of NH^3 which would provide a reduction atmosphere in addition to carried out nitridation. HCl (1.0 M) was added into the SiO_2 to act as a mineralizer and break it up [9]. The reactor bomb was made of SS-316 stainless steel whose cylindrical primary body was 80 mm in outer breadth, 55 mm in inner width and 95 mm in length. The spread has inward screw strings and the primary body has external screw strings, so that could screw tight. The top screw front of the primary body was 80 mm in outside distance across, 43mm in inward breadth, and 43mm in height. The viable warming area of the radiator was one-third from the base of the chamber, and the upper area of the barrel was normally cooled.

Synthesis of silicon nitrides; SNA, SNB, SNC and SND

Approximately 25 grams of rice husk ash were soaked in HCl (1.0 M) for 3 hours, it was filtered and transferred to a bomb calorimeter, 5 grams of sugarcane bagasse ash and 150 mL of 28% ammonium hydroxide (NH_4OH) were added to the mixture. Teflon was wrapped around the threads before the bomb was tightly closed. The bomb calorimeter was heated at 100°C in thermostat-controlled furnace for 24hrs. The content was allowed to cool and then the resulting residue filtered using Whatman No 1 Filter paper. The solid residue of silicon nitride was labeled SNA, the procedure was repeated at 150°C, 200°C, 300°C to give SNB, SNC, and SND. SNB and SNC were washed with distilled water and dried to account weight. The instruments used for characterization were XRD (Model D2 Phaser, Bruker AXS, Germany), XRF 200 compact, FTIR-8400 Spectrophotometer. Other equipment's were Electric weighing balance (ATX224Shimadzu), Bomb calorimeter.

Results and Discussions

Elemental analysis

The composition of major element oxides present in the SNA, SNB, SNC, and SND were determined using the X-ray Fluorescence (XRF) technique and are shown in Table 1.

We used XRF in elemental analysis, but it gives the result in oxide form in small amount because it is leach, some metallic oxide were not detected by XRF, such as copper oxide and nickel oxide, but MgO was detected but was zero. XRF cannot detect nitrogen, it can only detect element with an atomic number above 11, that why we further used FTIR and XRD.

As shown in the table, the percentages of Cl were found to be higher in SND and SNA at 4.51 and 3.48 than in SNB and SNC at 1.73 and 1.79 respectively. This is attributed to the pretreatment of the products after synthesis. Whereas, all the products (SNA, SNB, SNC and SND) were leached with 1.0 M HCl, SNB and SNC were washed with distilled water after leaching; the SNA and SND were not. Leaching with HCl leads to material having high level of chloride while distilled water removes the surface chlorides as observed by Baris [3]. Consequently, XRF analysis showed that SNB and SNC had higher silica percentage at 94.19 and 93.47 compared to SND and SNA at 90.69 and 90.10 % respectively.

It is clear that the major component of the silicon nitride is Si. However, other elements seen include Aluminium, alkali metals, alkaline earth metals, iron and phosphorus, and they are all in small amounts.

Characterization of synthesized silicon nitride by FTIR

Figures 1, 2, 3 and 4 show FTIR spectra of silicon nitrides SNA, SNB, SNC and SND, respectively synthesized at various temperatures of 100, 150, 200, 300°C.

The temperature for synthesis is low because it is hydrothermal process involving water, and we consider the saturated vapour pressure of water that is why the temperature is low, 100°C, 150°C, 200°C and 300°C.

The FTIR spectra of SNA which was synthesized at 100°C shows absorption band at 411.8, 470.6, 610.4, 671.2,

702.0, 803.3, 920.9, 1073.1 and 1400.2 cm^{-1}. The absorption band at 470.6 cm^{-1} is attributed to Si-N (stretching), at this wave-number, there is overlap of Si-O with Si-N, implying amorphous phase [9]. A weak band at 671.2 cm^{-1} which is characteristic of a silicon nitride Si-N-Si stretching vibrations was observed [11]. The bands at 803.3 cm^{-1} and 1107.1 cm^{-1} are attributed to the Si-C and Si-O-Si, respectively.

The FTIR spectra of SNB, SNC and SND are similar to that of SNA. However, figure 2 shows a clearer overlap of Si-O and Si-N vibrations at 470.6 cm^{-1}, due to the overlap, can assume that it may be present in amorphous phase and covered by Si-O bonding [9].

The FTIR spectrum of SNC which was synthesized at 200°C is shown in figure 3. Remarkably, the band at 574.7cm^{-1} similar to that reported by Takase and Tani as originating from Si-N vibrations attributed to α-silicon nitride [12]. The absorption band at 1110.0 cm^{-1} is attributed to Si-O-Si bonding while the characteristics stretching vibration band of silicon nitride were observed at 669.3 cm^{-1} [9,11]. The broad peak at 791 cm^{-1} show an overlap of Si-C in addition to Si-O and Si-N vibration observed at 464.6 cm^{-1}.

The spectrum of SND, synthesized at 300°C is shown in figure 4. As observed from FTIR spectra of the four silicon nitride materials, the spectral peaks become sharper as synthesis temperature was increased from 100 to 300°C as reported by Chen. Further bands at 477.3 cm^{-1} and 791.7 cm^{-1} related to overlapping (Si-O and Si-N) and (Si-N and Si-C) vibrations, become more resolved. Therefore, the FTIR confirms the synthesis of silicon nitride [13].

X-ray diffractions

Characterizations and phase analysis of adsorbent material was done using x-ray diffractions. The diffractogram of SNA is presented by figure 5.

The phase matches identified for SNA adsorbent material correspond to α-silicon nitride and β-silicon nitride. The degree of crystallinity was determined using the procedure reported by Sanjeeva [14]. The material had a degree of crystallinity of 64.28 wt% and 35.27 wt% amorphous. These values for the percentage crystallinity indicate semi crystallinity [15]. The material contained a

Nitride	SiO_2	Cl	Al_2O_3	P_2O_5	CaO	K_2O	Fe_2O_3	CuO	NiO	Cr_2O_3	MgO
SNA	90.10	3.48	1.67	0.56	0.85	0.40	1.82	0.29	0.29	0.19	0.00
SNB	94.19	1.73	1.19	0.20	0.33	0.37	0.55	ND	ND	ND	1.161
SNC	93.47	1.79	1.41	0.19	0.43	0.34	0.92	ND	ND	ND	1.08
SND	90.69	4.51	0.97	0.33	0.55	0.43	0.93	ND	0.11	0.12	0.98

Table 1: Chemical composition of silicon nitrides SNA, SNB, SNC and SND

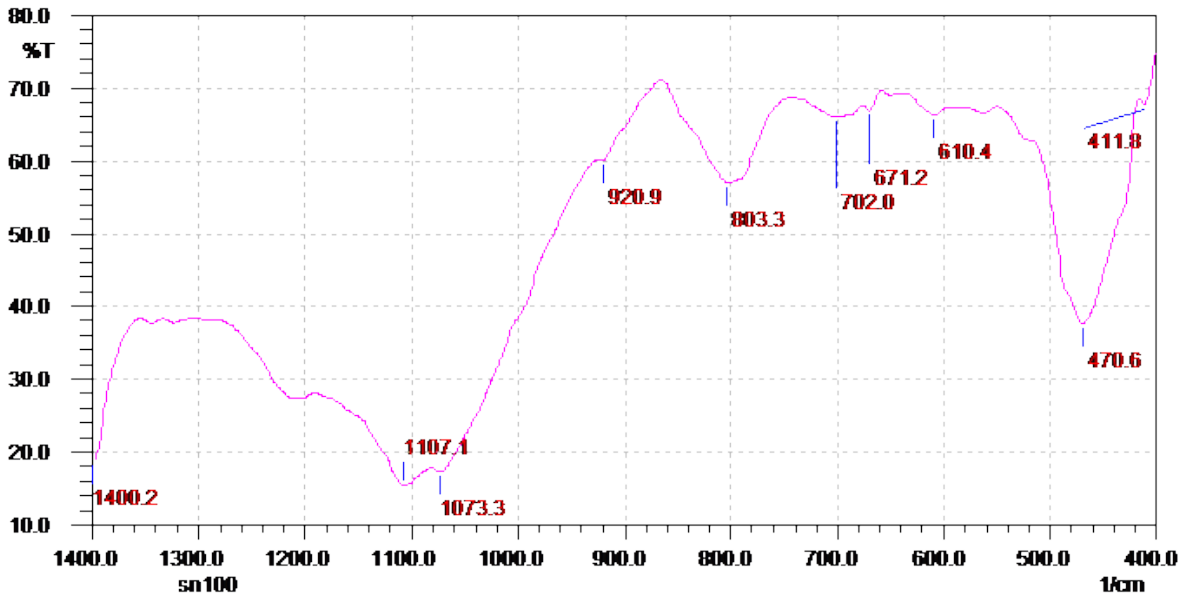

Figure 1: FTIR spectrum of silicon nitride, SNA synthesized at 100°C

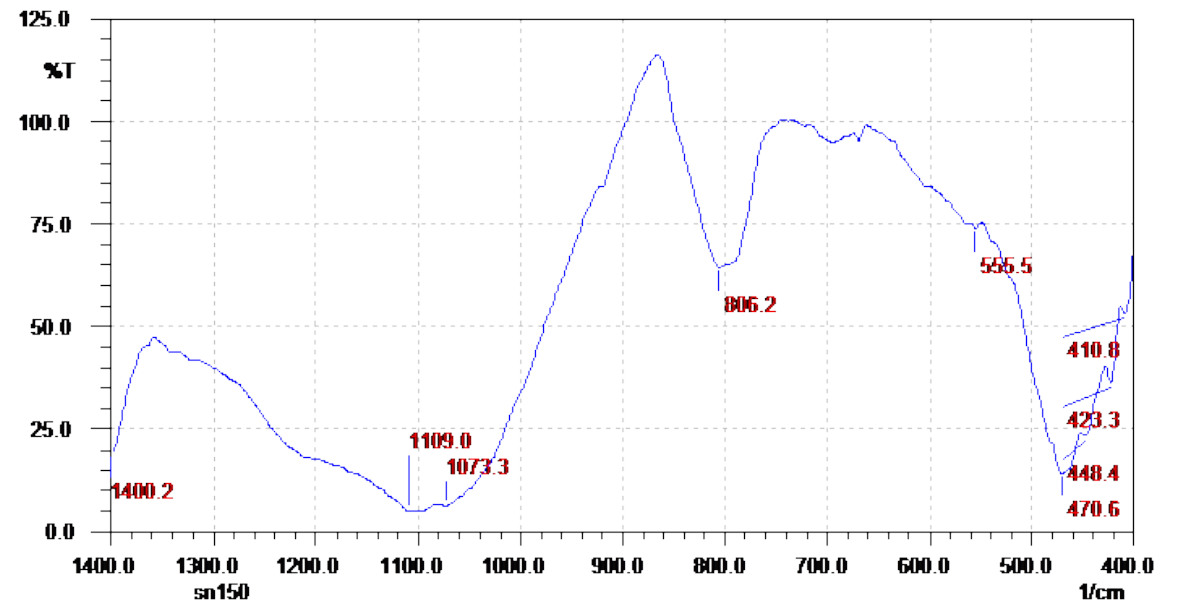

Figure 2: FTIR spectrum of silicon nitride, SNB synthesized at 150°C

higher percentage of α-phase (64.6%) of silicon nitride as compared to the β-phase (27.8%) as implied by figure 5.

Although SNA was synthesized hydrothermally at 100˚C for 24 hours, a relatively lower temperature when compared to others in literature, the result agrees with the findings of Chen [9] who reported that the peaks of SiC and Si_3N_4 get sharper and stronger as temperature increases. Chen's work found out that the percentage of crystallinity reduced with increase in the duration of synthesis while lattice twisting increased as the reaction temperature was increased. The Si-bond absorbed more nitrogen under NH_4OH condition which leads to the broadening of the peak. Moreover, it was observed that increase in reaction temperature of 300˚C made all of the peaks sharper and broader as compared to those of the product synthesized at 250˚C. Therefore, we can conclude that increase in temperature and duration helps in the formation of Si_3N_4 and SiC.

Conclusion

With respect to the results obtained from this study, the following conclusions can be made; the rice husk contained high amount silica with minute impurities. Silicon nitride was successfully synthesized from rice husk and sugarcane bagasse ashes by hydrothermal process at various temperatures of 100°C, 150˚C, 200˚C and 300˚C for 24 hrs.

Water washing and acid leaching steps was proved to be a valid method for obtaining high purity rice husks containing almost only C and SiO_2. Weight percentage of Si_3N_4 in the products was found to be increasing with increasing reaction duration. SNA was analyzed as Si_3N_4, rich in α-phase, by XRD analysis.

FTIR only gives the functional group present in each sample, that is why the peaks in all samples are almost similar, but XRD can further tell you on the phase present in the sample, we therefore say XRD give best characterization method used in this work.

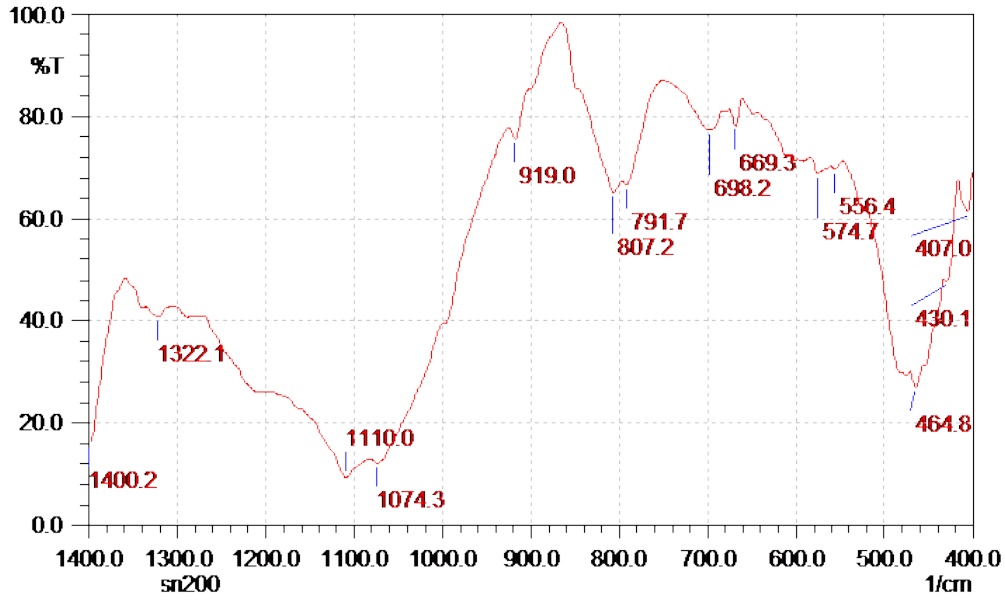

Figure 3: FTIR spectrum of silicon nitride SNC synthesized at 200°C

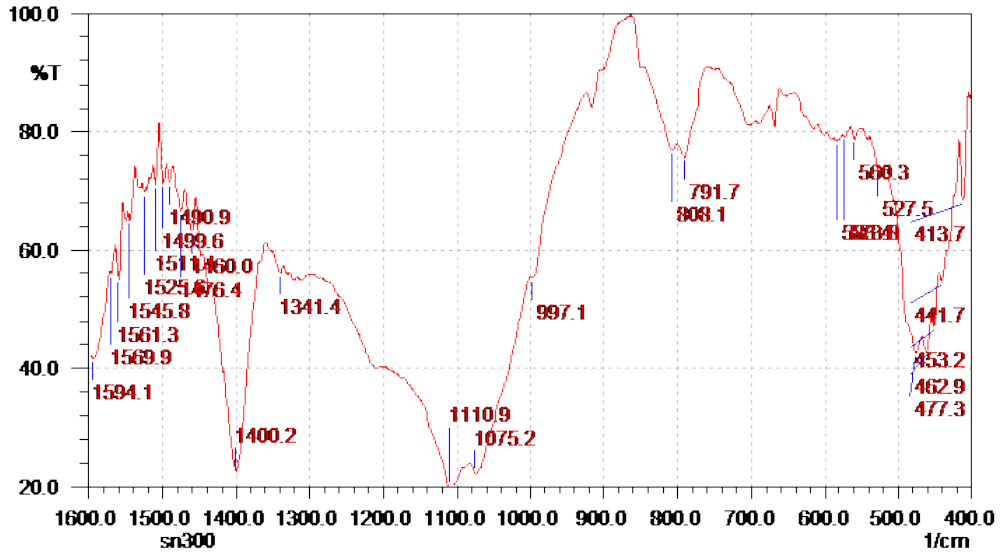

Figure 4: FTIR spectrum of synthesized silicon nitride at 300°C

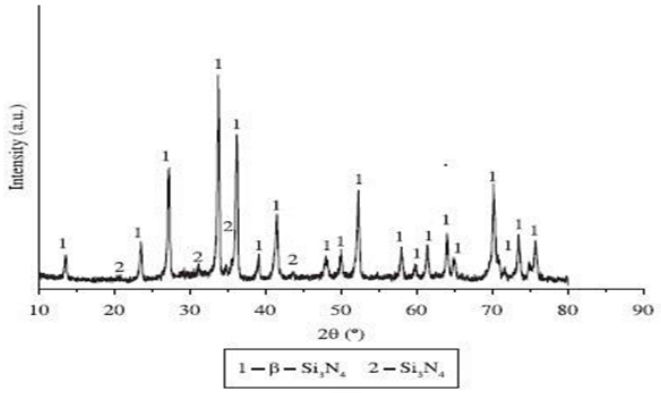

Figure 5: XRD pattern of adsorbent SNA. 1 is α-silicon nitride while 2 is β-silicon nitride

Acknowledgement

Wewould use this opportunity to thank the Kenyatta University Chemistry Department staff and laboratory technicians for their support during this research.

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